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(54) CARBON ELECTRODE FOR GENERATING FLUORINE GAS OR NITROGEN TRIFLUORIDE GAS AND DEVICE FOR GENERATING FLUORINE GAS OR NITROGEN TRIFLUORIDE GAS USING THE ELECTRODE

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a carbon electrode for manufacturing high-purity F2 or NF3 having a low content of CF4 and supply the F2 or NF3 on-site and a device for generating the high-purity F2 or NF3 using the electrode as a first purpose and to furnish a carbon electrode for suppressing the polarization due to an anode effect in electrolysis and generating the F2 or NF3 to be stably supplied on-site and a device for generating high-purity F2 or NF3 using the electrode.
SOLUTION: A carbonaceous material high in bonding strength between the carbon particles and with the bonding strength measured at ≥0.2 (g/mm3) by the ACT-JP method is used as the carbon electrode for generating high-purity F2 or NF3 to suppress the generation of CF4. Further, a metal fluoride is added to the carbonaceous material to increase the bonding strength between carbon particles, and the polarization due to anodization is controlled.

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* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1] The fluorine gas or the carbon electrode for the 3 nitrogen-fluoride generation of gas of a high grade whose value which said carbon electrode measured by the ACT-JP method by the following conditions it is a carbon electrode for generating the fluorine gas or 3 nitrogen-fluoride gas of a high grade, and is more than 0.2 (g/mm3).
Diameter of an injection nozzle : 5.2mm injection material : Alumina air-current pressure : 5kg/cm2 injection material incident angle : The flow rate of 90 degree injection air current: Amount of 390cm3 / min injection material : Distance from 70g [/] time injection nozzle to a sample front face: It is [Claim 2] 100mm. The fluorine gas or the carbon electrode for the 3 nitrogen-fluoride generation of gas whose content of the two-component system metal fluoride which consists of said lithium fluoride and said metal fluoride it is the fluorine gas or the carbon electrode for the 3 nitrogen-fluoride generation of gas which consists of a carbonaceous ingredient, lithium fluoride, and a metal fluoride with the melting point more than the burning temperature of a carbonaceous ingredient, and is 0.1 to 5 mass %.
[Claim 3] The fluorine gas according to claim 2 or the carbon electrode for the 3 nitrogen-fluoride generation of gas where said metal fluoride consists of at least one or more sorts of things chosen from from among a calcium fluoride, magnesium fluoride, barium fluoride, aluminum fluoride, and a fluoride lanthanum.
[Claim 4] The fluorine gas or the carbon electrode for the 3 nitrogen-fluoride generation of gas of a high grade according to claim 2 or 3 whose value measured by the ACT-JP method by said conditions is more than 0.2 (g/mm3).
[Claim 5] The fluorine gas or the 3 nitrogen-fluoride gas generator which contained fluorine gas according to claim 1 to 4 or the cell using the carbon electrode for the 3 nitrogen-fluoride generation of gas in the container for ambient atmosphere control.
[Claim 6] The fluorine gas according to claim 5 or the 3 nitrogen-fluoride gas generator with which a storage means to store the fluorine gas or 3 nitrogen-fluoride gas which occurred was established.
[Claim 7] The fluorine gas according to claim 5 or 6 or the 3 nitrogen-fluoride gas generator whose carbon tetrafluoride gas contained in said fluorine gas which occurred, or 3 nitrogen-fluoride gas is 20 ppm or less.

[Translation done.]

* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the fluorine gas or the 3 nitrogen-fluoride gas generator which used fluorine gas or the carbon electrode for the 3 nitrogen-fluoride generation of gas, and it. Especially, the fluorine gas or 3 nitrogen-fluoride gas of a high grade with little generating of carbon tetrafluoride gas can be generated stably, and the anode effect is controlled and fluorine gas or 3 nitrogen-fluoride gas can be generated stably. On-site It is related with the fluorine gas or the 3 nitrogen-fluoride gas generator using the fluorine gas which can supply fluorine gas or 3 nitrogen-fluoride gas to a semi-conductor manufacturing facility etc. or the carbon electrode for the 3 nitrogen-fluoride generation of gas, and it.
[0002]
[Description of the Prior Art] Potassium-fluoride-hydrogen fluoride system (henceforth KF-HF system) mixing fused salt is used as the electrolytic solution, and a carbon electrode is used for fluorine gas (henceforth F2), and it electrolyzes into an anode plate and is manufactured.
[0003] Moreover, 3 nitrogen-fluoride gas (henceforth NF3) electrolyzes ammonium fluoride-hydrogen fluoride system (henceforth NH4 F-HF system) mixing fused salt using a nickel (henceforth nickel) anode plate, and is manufactured.
[0004] The former and these [F2] NF3 Only a complement is usually supplied to a semi-conductor manufacturing facility from a bomb, and it is used for washing of semi-conductor components etc. However, it is especially the high grade NF 3. There was a problem that productivity could not supply adequately bad. Therefore, it might be influenced more of semi-conductor manufacture stopping etc. often insufficient [supply of NF3]. In order to avoid this, expensive gas needed to be stored preparatorily and so much. Moreover, F2 Even if it attaches, it is high-pressure F2 of a bomb outlet part. There was a corrosion problem to depend and there was a case where leakage of gas harmful during storage was produced.
[0005] Therefore, recently comes, it sets to a semi-conductor manufacturing facility, and they are these [F2] because of washing, such as semi-conductor components. NF3 They are these [F2] at the on-site which can always use the amount of requests. NF3 The equipment which can be generated is demanded.
[0006] However, F2 NF3 When nickel anode plate was used for generating, the dissolution of an anode plate needed to take place during electrolysis, nickel ion an electrode is not only exhausted, but eluted needed to become the sludge of a fluoride, it needed to precipitate at the bottom of a cell, and the sludge needed to be removed periodically. Moreover, these [F2] NF3 Since the so-called anode effect that an electrical potential difference goes abruptly up suddenly according to a polarization operation occurred when a carbon electrode is used for generating, operation with high current density was difficult. Therefore, these [F2] NF3 It was difficult to have made it generate on-site.
[0007] For example, NF3 In the fused salt of a NH4 F-HF system, since the vapor pressure of HF is high, HF invades between the layers of the detailed lamellar crystal which exists in the grain boundary of a carbon particle, or a carbon particle, and using a carbon electrode for manufacture produces omission of the carbon particle which constitutes a lifting carbon

electrode for distortion or a local collapse in a carbon electrode, although indicated by JP,5-70982,A and this Taira No. 86490 [five to] official report. The carbon particle which dropped out in the cell is F2 generated. It reacts, becomes carbon tetrafluoride gas (henceforth CF4), and is NF3. It mixes. NF3 CF4 The boiling point is CF4 used abundantly as the dry etching gases for semi-conductor manufacture, or cleaning gas of a CVD system since it is very near and distillation separation cannot be performed. High grade NF 3 with few contents There is a problem that it is not obtained.

[0008] Electrolysis of extent which will also have been set to the carbon electrode if the KF-NH4 F-HF system fused salt which added KF is used in order to lower the vapor pressure of HF is NF3 besides the problem of the anode effect too, although it is possible. Compared with the case where generation current efficiency uses a nickel anode, it is low, and has not resulted even in utilization.

[0009] As a way stage for controlling the anode effect, the example using the electrode which sank in into the pore of a carbon electrode is indicated by JP,2-47297,A in the metal fluoride. However, in order to prevent the oxidative consumption of a carbon electrode or an equipment component, it must permute by inert gas ambient atmospheres, such as nitrogen gas (henceforth N2), as a result large-sized pressurization heating apparatus (HIP equipment etc.) are not only required to sink in a metal fluoride into the pore of a carbon electrode, but it has been a problem in respect of workability, the manufacture period, and the manufacturing cost.

[0010] Moreover, the method of making the ground carbonaceous aggregate mix a metal fluoride as other approaches is indicated in JP,61-12994,B. According to this, a large-scale facility of saturator etc. is not needed but it can be said that it excels also in cost. However, it was very difficult it to disperse and disappear at the baking process of carbon material to the burning temperature of carbon material being 900-1000 degrees C, since it begins to fuse LiF above about 850 degrees C, and to have made it contain in a carbon material by this approach.

[0011]

[Problem(s) to be Solved by the Invention] Then, this invention is CF4. F2 of a high grade with few contents, and NF3 It can manufacture and they are these [F2]. Or NF3 F2 of the high grade for supplying stably on-site Or NF3 F2 of the high grade using the carbon electrode for generating, and it Or NF3 It sets it as the 1st purpose to offer a generator. Moreover, polarization by the anode effect at the time of electrolysis is controlled, and it is F2. Or NF3 F2 supplied stably on-site Or F2 of the high grade using the carbon electrode for NF3 generating, and it Or NF3 It sets it as the 2nd purpose to offer a generator.

[0012]

[Means for Solving the Problem] Then, this invention persons are CF4 first. As a result of adding examination about a means to prevent generating, it is CF4 by using the high carbonaceous ingredient of the bonding strength between carbon electrodes with few omission of a carbon particle, i.e., a carbon particle. The knowledge of the ability to control generating was carried out. Furthermore, it found out that the bonding strength between carbon particles had the close relation to the measured value by the ACT-JP method. Then, this invention persons are F2 of a high grade by optimizing the measured value by the ACT-JP method of a carbonaceous ingredient. Or NF3 It comes to complete header this invention for the ability to do with the carbon electrode which consists of a carbonaceous ingredient which can be generated. That is, this invention is F2 of the high grade whose value measured by the ACT-JP method is more than 0.2 (g/mm3). Or NF3 Let the carbon electrode for generating be a summary.

[0013] The technical problem biggest by this invention is F2 for which it asks. NF3 CF4 mixed in inside as a by-product It is controlling mixing. This CF4 It is generated mainly by following the (1) type.

C+2F2 ->CF4 .... (1)

(1) CF4 in a formula HF trespasses upon the pore and the grain boundary of carbon material during electrolysis, the electrolysis reaction of HF arises there, and it is F2. It is generated by generating. Namely, CF4 which the size of the bonding strength between particles of the ingredient origin held when the raw material (aggregate) of a carbonaceous ingredient is calcinated showed by (1) formula It becomes the index of the ease of being generated.

Therefore, the method of evaluating the aforementioned bonding strength between particles is needed. Although the degree of hardness (for example, shore hardness) of a carbonaceous ingredient is a parameter generally used in case it evaluates the workability of an ingredient, it is unsuitable as the evaluation approach of evaluating the bonding strength between carbon particles as used in the field of this invention.

[0014] Then, this invention persons are Arata style coat appraisal methods (as a result of applying ArataCoating Test with Jet Particles (the ACT-JP method) to this system and performing systematic examination, the knowledge of this method being an approach that the bonding strength between particles of a carbonaceous ingredient can be evaluated was carried out.) generally [in case the bonding strength between particles of a ceramic-flame-spraying coat with the structure which a raw material particle superimposes is evaluated] used. The ACT-JP method is one of the injection type test methods, and is an approach of evaluating the bonding strength between particles of a thermal-spraying coat using the wear rate of a coat, by changing whenever [exposure rate or illuminating-angle] into a thermal-spraying coat, spraying a ceramic particle, and measuring the degree (weight reduction) of the wear under each conditions. Although the production approaches differ, if a common carbonaceous ingredient (carbon Plastic solid which consists of the carbonaceous aggregate and a binder), and a thermal-spraying coat are seen as what the particle combined, it can be considered that these are the same. From the wear device in the ACT-JP method, the wear rate of a test piece is detected as bonding strength between particles. And a wear rate decreases, so that the bonding strength between particles is large. In the ACT-JP method, the ACT-JP value was defined as follows and this value estimated.

ACT-JP value = 1-/MV .... (2)

MV : wear rate of the test piece in a stationary wear condition (mm3/g)

MV =(1000 and W1)/(rho-W 0) .... (3)

rho: Bulk density of a test piece (carbon base material) (g/cm3)

W0 : Amount of the injection material (alumina powder of 60 meshes) used for the ACT-JP trial (g)

W1 : Abrasion loss of the test piece (carbon base material) in a stationary wear condition (g)

The abrasion loss of a test piece changes with jet velocity, and corresponds only in an include angle also with a fixed ACT-JP value here. That is, if the incident angle to the test piece of an alumina particle becomes smaller than 90 degrees, wear will be produced between an alumina particle and a test piece front face. In order to evaluate the bonding strength between particles of the particle which constitutes the carbon material which originally serves as a test piece, all the kinetic energy of an alumina particle must be spent on the cleavage of the particle which constitutes the carbon base material which is a test piece. Therefore, as for the incident angle to the test piece of an alumina particle, considering as 90 degrees is desirable.

[0015] the so-called duality which adds and calcinated [kneaded, fabricated and] binding material, such as a coal-tar pitch, to this as the manufacture approach of the carbon electrode concerning this invention, using corks, such as petroleum coke and pitch coke, as the carbonaceous aggregate -- the carbon Plastic solid of a system of 1 yuan which fabricated the carbon Plastic solid and deterioration pitch of a system, and the meso carbon micro bead, and was calcinated can be used. for example, duality -- as the carbonaceous aggregate, the carbon Plastic solid of a system mixes corks, such as petroleum coke and pitch coke, by predetermined combination, the mixed carbonaceous aggregate and binding material, such as coal-tar pitch of tales doses, are added, it mixes, and it performs CIP shaping by pressure 50-100MPa, and calcinates and fabricates it at 900-1100 degrees C after processing a predetermined configuration. Moreover, the carbon Plastic solid of a 1 yuan system performs CIP shaping by pressure 50-100MPa, and calcinates and fabricates a deterioration pitch and a meso carbon micro bead at 900-1100 degrees C after processing a predetermined configuration. and the case of the carbon Plastic solid of a 1 yuan system -- a pressure -- adjusting -- moreover, duality -- in the case of the carbon Plastic solid of a system, it is desirable to adjust the compounding ratio of a pressure and the carbonaceous aggregate suitably, to adjust so that the measured value by the ACT-JP method may become more than 0.25 (g/mm3) preferably more than 0.2

(g/mm3), and to use it as an electrode.
[0016] Also in itself, the above-mentioned carbon material is low polarizability in KF-2HF, and is CF4. It is a content F2 of a high grade 20 ppm or less Or NF3 It can be made to generate.
[0017] In order to raise the polarization property by the anode effect under electrolysis (it is made hard to polarize) Moreover, LiF, A calcium fluoride with the melting point more than the burning temperature of a carbonaceous ingredient (it is hereafter called CaF2.) Magnesium fluoride (it is hereafter called MgF2.) Barium fluoride (it is hereafter called BaF2.) Aluminum fluoride (it is hereafter called AlF3.) Fluoride lanthanum (LaF3 is said hereafter.) Carry out specified quantity mixing of at least one or more sorts chosen from inside, and it heats until the bi-phase of a metal fluoride with the melting point more than the burning temperature of LiF and these carbonaceous ingredient turns into the liquid phase. It grinds after cooling, specified quantity addition is carried out at the above-mentioned carbonaceous aggregate, and the two-component system metal fluoride content carbon material which consists of a metal fluoride with the melting point more than the burning temperature of LiF and a carbonaceous ingredient is obtained by calcinating at 900-1000 degrees C after shaping (CIP etc.). It distributes well in a carbonaceous ingredient, without being in the condition that the metal fluoride with high LiF and melting point joined together, and LiF dispersing during carbonaceous ingredient baking, even if the surroundings of a metal fluoride particle with the high melting point will be able to be turned [to which it comes by LiF], will be mixed into a carbonaceous ingredient and will calcinate at 900-1000 degrees C, if it does in this way. By this, the bonding strength between the carbon particles of the electrode which consists of a carbonaceous ingredient increases, and the polarization by the anode effect can be controlled. In addition, as for the mixed rate of a metal fluoride with the melting point more than the burning temperature of the carbonaceous ingredient combined with LiF, the optimal range exists to the purpose. When the rate of LiF increased, the melting point becomes 1000 degrees C or less and a carbonaceous ingredient is calcinated, this mixture cannot be made to contain in a carbonaceous ingredient. Moreover, if the mixed rate of LiF decreases too much, a polarization property will worsen (being easy to polarize). Therefore, as for the mixed rate of LiF and a metal fluoride, it is desirable to make LiF into 20 - 40%, and to use the remainder (80 - 60%) as a metal fluoride with the melting point more than the burning temperature of a carbonaceous ingredient. When it furthermore adds, as a metal fluoride with the melting point more than the burning temperature of the carbonaceous ingredient combined with LiF, they are LiF-CaF2 and LiF-MgF2. Combination is desirable. Thus, the bonding strength between carbon particles is heightened and the two-component system metal fluoride content carbon electrode which processes into an electrode configuration the metal fluoride content carbon material which controlled the polarization by the anode effect, and is built over this invention is obtained.
[0018] Thus, the obtained two-component system metal fluoride content carbon electrode has precise structure, the rate of an open pore is about 2 - 20%, and an average pore radius is about 0.1-1.0 micrometers. The content of the two-component system metal fluoride which the carbonaceous aggregate is made to mix adjusts loadings suitably so that it may finally become 0.1 - 5 mass % to a carbon electrode. Since the fall of the moldability of a carbon Plastic solid or reinforcement will be caused if there is no effectiveness in control of a polarization property when there is less content of a two-component system metal fluoride than 0.1%, and it increases more than 5%, it is not desirable.
[0019] Moreover, to the current-carrying part of the electrode which consists only of the above-mentioned carbonaceous ingredient, and a two-component system metal fluoride content carbon electrode, by performing covering of nickel or copper (henceforth Cu) by the approach of arbitration, such as thermal spraying and electrolytic plating, contact of a busbar part serves as a metal-metal, as a result the increment in electric contact resistance with time can be controlled. This is desirable in order to make an electrode life live long. Furthermore, the one-sheet electrode [one sheet] current value to share becomes uniform, and stable operation can be secured.
[0020] By doing in this way, it is F2 of a high grade. Or NF3 It can consider as the carbon electrode which can be supplied stably. Moreover, F2 by the on-site which can use as the

carbon electrode which controlled polarization by the anode effect, and can be formed successively to a semi-conductor facility etc. Or NF3 It can consider as a generator.
[0021] Next, this electrode is used and it is F2 at on-site. Or NF3 The generator which can be generated stably is explained. Drawing 1 is F2. Or NF3 It is the mimetic diagram of a generator. Mild steel is used and, as for the body 1 of a cell, the electrolytic solution 2 of KF-2HF or KF-NH4-2HF is contained in this. Moreover, the gaseous-phase part is separated into the anode plate room 12 and the cathode room 13 by the skirt board 10 made from a Monel metal. The anode plate room 12 is equipped with the carbon electrode 3 concerning this invention, and it is F2 from this front face at the time of electrolysis. Or NF3 It generates. The nickel cathode 5 is located at the cathode room 13, and it is F2. Or NF3 It is H2 from this front face also at the time of electrolysis [which]. Gas 6 occurs. The gas 4 and 6 which occurred flows out of the uptake openings 8 and 9, respectively. H2 Gas 6 is introduced to the exclusion equipment which is not illustrated. F2 Or NF3 the sodium fluoride (henceforth NaF) attached for the purpose of HF exclusion -- it is introduced into the following system through a column 11. sintering Monel for removing the particle generated by the entrainment of the electrolytic solution, although not illustrated depending on the case, or the filter made from sintering Hastelloy -- NaF -- you may prepare in the downstream of a column 11. The unnecessary gas in equipment is N2. Exhaust air processing is carried out out of equipment using a bomb 7. In the case of NF3 generating, N2, O2, and a dinitrogen oxide (henceforth N2 O) mainly generate as unnecessary gas. Among these, N2 O is removable by passing water, N2 O column, and a sodium thiosulfate. O2 Activated carbon removes.
[0022] Thus, F2 generated Or NF3 When using it under reduced pressure, reduced pressure Rhine 14 is used. The pressure regulating valve 15, the storage means 17 under reduced pressure (henceforth a buffer tank), the pressure gage 18, and the vacuum pump 30 grade are prepared in Rhine. Pressure control is carried out with a vacuum pump 30, the pressure is regulated with a pressure gage 18 and valves 16 or 19, and the buffer tank 17 is F2. Or NF3 Receipts and payments of gas are controlled. A pressure regulating valve 15 prevents that the inside of the body 1 of a cell is decompressed. And F2 Or NF3 In case it is used, it takes out from an outlet 20.
[0023] F2 Or NF3 In case it is used under pressurization, pressurization Rhine 21 is used. A pressure regulating valve 22, a pressurizer 23, the buffer tank 25 used as a storage means, the pressure gage 26, the flowmeter 28 with a flow regulation function (henceforth mass flow), and the vacuum pump 30 are formed in Rhine. The gas which occurred from the body 1 of a cell is pressurized with a pressurizer 23. At this time, a pressure regulating valve 22 prevents that the inside of the body 1 of a cell is decompressed. The buffer tank 25 controls receipts and payments of gas by the pressure gage 26, valves 24 and 27, and mass flow 28. And F2 In case it is used, it takes out from an outlet 29. F2 generated by electrolysis in this invention Or NF3 a means to store is established and it is the need by this -- by the way -- F2 of the amount of requests Or NF3 It can provide. In addition, these reduced pressure Rhine or pressurization Rhine is F2 which can be arranged suitably and starts this invention. Or NF3 A generator is not limited to these.
[0024] Generation gas F2 And NF3 CF4 to mix The stowage container which contains the body 1 of a cell in order to make it decrease further (It is hereafter called a cabinet.) 31 is arranged and they are N2 and argon gas (it is hereafter called Ar.). etc. -- the carbon dioxide in the air which causes CF4 generating by carrying out an ambient atmosphere permutation by rare gas (it is hereafter called CO2.) Moisture etc. can be eliminated. By this, it is F2 of a high grade. And NF3 It can generate.
[0025] The anode effect developmental mechanics produced peculiar to a carbon electrode is considered as follows. That is, in the usual electrolysis, it is easy to produce the graphite fluoride other than a formula (4) in an electrode surface by the formula (5). Although graphite fluoride is pyrolyzed by the formula (6), if the rate of a formula (5) becomes larger than the rate of a formula (6), in order for graphite fluoride to exist, the wettability of an electrode and the electrolytic solution will worsen. consequently -- since the area in contact with the electrolytic solution decreases and current density becomes very high compared with the apparent value --

a polarization operation -- large -- becoming -- just -- being alike -- it comes to produce the anode effect.

C+HF2--> -- C 11 / 2F2+HF10e-.... (4)

nC+nHF2--> (CF) n 10 nHF+ne -.... (5)

4 CF->CF4+3C .... (6)

However, if molecule-like LiF exists in the interface of a carbon electrode and the electrolytic solution, a fluorine-graphite lamellar compound (CX+F-) will generate easily by the reaction of the following formula (7). Since [with sufficient conductivity] this compound has high surface energy, it is well damp in the electrolytic solution. Moreover, HF in the electrolytic solution discharges on the intercalation compound generated as shown in the formula (6), and it is F2. It generates.

XC+HF2 -> (CX+F-) 10HF10e-.... (7)

(CX+F-)+HF2 -- -> (CX+F-) 11 / 2F2+HF10e-.... (8)

Thus, LiF acts as a catalyst of a fluorine-graphite lamellar compound generation reaction, and the operation is F2. Electrolysis and NF3 In order to show the same effectiveness also in electrolysis, the metal fluoride content carbon electrode of this invention is F2. NF3 It becomes possible to control polarization, a crack, etc. by the anode effect at the time of generating, and is F2. NF3 It is applicable to any electrolysis. However, NF3 In the case of an electrolysis composition reaction, it is NF3, especially when it is the reaction shown in the formula (9) and uses a carbon electrode. It was a big technical problem on industry that generation current efficiency is low.

NH4 F+6HF2-->NF3 1010HF16e .... (9)

In the case of a carbon electrode, it is NH4+ in order for graphite fluoride with very low surface energy to generate to an electrode surface by the reaction shown in the formula (5). NF3 which it becomes impossible to have stuck to up to an electrode surface, and was shown in the formula (9) Generation current efficiency becomes low. However, if the carbon electrode concerning this invention is used as an anode plate, the fluorine-graphite lamellar compound shown in the formula (7) will arise, electrode surface energy does not fall like the conventional electrode, but it is NH4+. Adsorption becomes possible and it is NF3. Generation current efficiency rises. The electrode concerning this invention is CF4 as there are few particle omission even if the bonding strength between particles is large and a fluorine-graphite lamellar compound arises near the front face, and shown by the formula (1). There is very little generation. For this reason, CF4 to mix It is called 20 ppm or less, it reaches to an extreme, and is F2 of a high grade. Or NF3 It has the description of being obtained.

[0026] Next, since it is small, the gas pressure generated from a cell is [1.0kPa extent and] F2 to the system of reaction or a processor. Or NF3 The devising point at the time of supplying is explained. This equipment has Rhine 14 or 21 which supplies these gas to a reduced pressure system or a pressurization system as shown in drawing 1 . Fundamentally, when pressure regulating valves 15 or 22 are decompressed from 0.5kPa(s), it closes, and if the pressure of Rhine including the anode plate room 12 and the HF absorption tower 11 reaches ordinary pressure, pressure regulating valves 15 or 22 will open, and gas supply will be started. If the gas of the specified quantity is the buffer tank 17 of a reduced pressure system, and a pressurization system by repeating this actuation, the buffer tank 25 will be covered via a pressurizer 23. What is necessary is just to attach Rhine of which format which suited the application, although Rhine which holds the both system of a reduced pressure system and a pressurization system was shown here. These invention has the greatest description at the point which can supply the gas which was not able to be supplied when it was not a bomb conventionally to the system of reaction or a processor at on-site using a cell. Especially, it is F2 of a high grade. NF3 It can be used suitable also for the semi-conductor manufacture field and the liquid crystal field as which gas is required.

[0027]

[Example] Although this invention is concretely explained based on an example below, this invention is not limited to these examples.

[0028] (Example 1) the meso carbon micro bead whose mean particle diameter is 10 micrometers

-- CIP -- it calcinated at 900 degrees C after pressing by law at 30MPa(s), and the carbon burned product of 300x300x500 (mm) was obtained.
[0029] (Example 2) The carbon burned product of 300x300x500 (mm) was obtained like the example 1 except having changed into 50MPa(s) the compacting pressure of the raw material used in the example 1.
[0030] (Example 3) The carbon burned product of 300x300x500 (mm) was obtained like the example 1 except having changed into 70MPa(s) the compacting pressure of the raw material used in the example 1.
[0031] (Example 4) The carbon burned product of 300x300x500 (mm) was obtained like the example 1 except having changed into 90MPa(s) the compacting pressure of the raw material used in the example 1.
[0032] (Example 1 of a comparison) The carbon burned product of 300x300x500 (mm) was obtained like the example 1 except having changed into 10MPa(s) the compacting pressure of the raw material used in the example 1.
[0033] (Example 5) The temporary-quenching pitch coke 75 mass section was blended with the petroleum system raw coke 25 mass section whose mean particle diameter is 10 micrometers, and the carbonaceous aggregate 100 mass section was obtained. After adding the coal-tar pitch 100 mass section which serves as binding material at this, it kneaded and CIP shaping was carried out by 90MPa. This Plastic solid was calcinated at 1000 degrees C, and the carbon burned product of 300x300x500 (mm) was obtained.
[0034] (Example 2 of a comparison) The carbon burned product of 300x300x500 (mm) was obtained like the example 5 except having set compacting pressure to 50MPa(s).
[0035] (Example 6) LiF whose mean particle diameter is 30 micrometers, and CaF2 whose mean particle diameter is 30 micrometers After mixing at a rate of 4:6 by the mole ratio and carrying out heating fusion at 1200 degrees C, it cooled to the room temperature, the jet mill ground, and the two-component system metal fluoride whose mean particle diameter is 10 micrometers was obtained. It mixed in the meso carbon micro bead 100 mass section which used this two-component system metal fluoride 3 mass section in the example 1, and it calcinated at 1000 degrees C after shaping by 90MPa(s) at CIP, and the two-component system metal fluoride content carbon burned product of 300x300x500 (mm) was obtained. The obtained burned product contained the two-component system metal fluoride 3%.
[0036] (Example 7) LiF and CaF2 The two-component system metal fluoride content carbon burned product of 300x300x500 (mm) was obtained like the example 6 except having changed the mixed mole ratio into 2:8. The obtained burned product contained the two-component system metal fluoride 3%.
[0037] (Example 8) It is CaF2 as a metal fluoride. It is MgF2 to instead of. The two-component system metal fluoride content carbon burned product of 300x300x500 (mm) was obtained like the example 6 except having used it. The obtained burned product contained the two-component system metal fluoride 3%.
[0038] (Example 9) LiF whose mean particle diameter is 30 micrometers, and CaF2 whose mean particle diameter is 30 micrometers After mixing at a rate of 4:6 by the mole ratio and carrying out heating fusion at 1200 degrees C, it cooled to the room temperature, the jet mill ground to 10 micrometers, and the two-component system metal fluoride was obtained. This two-component system metal fluoride 1 mass section was mixed with the carbonaceous aggregate 100 mass section of an example 5, the coal-tar pitch 100 mass section was added, after kneading, it calcinated at 950 degrees C after CIP shaping by 90MPa, and the two-component system metal fluoride content carbon burned product of 300x300x500 (mm) was obtained. The obtained burned product contained the two-component system metal fluoride 1%.
[0039] (Example 10) LiF whose mean particle diameter is 30 micrometers, and CaF2 whose mean particle diameter is 30 micrometers After mixing at a rate of 4:6 by the mole ratio and carrying out heating melting at 1200 degrees C, it cooled to the room temperature, the jet mill ground to 10 micrometers, and the two-component system metal fluoride was obtained. This two-component system metal fluoride 3 mass section was mixed with the carbonaceous aggregate 100 mass section of an example 5, the coal-tar pitch 100 mass section was added, after

kneading, it calcinated at 950 degrees C after CIP shaping by 90MPa, and the two-component system metal fluoride content carbon burned product of 300x300x500 (mm) was obtained. The obtained burned product contained the two-component system metal fluoride 3%.

[0040] (Example 11) LiF whose mean particle diameter is 30 micrometers, and CaF2 whose mean particle diameter is 30 micrometers After mixing at a rate of 4:6 by the mole ratio and carrying out heating melting at 1200 degrees C, it cooled to the room temperature, the jet mill ground to 10 micrometers, and the two-component system metal fluoride was obtained. This two-component system metal fluoride 5 mass section was mixed with the carbonaceous aggregate 100 mass section of an example 5, the coal-tar pitch 100 mass section was added, after kneading, it calcinated at 950 degrees C after CIP shaping by 90MPa, and the two-component system metal fluoride content carbon burned product of 300x300x500 (mm) was obtained. The obtained burned product contained the two-component system metal fluoride 5%.

[0041] (Example 12) LiF whose mean particle diameter is 30 micrometers, and CaF2 whose mean particle diameter is 30 micrometers After mixing at a rate of 4:6 by the mole ratio and carrying out heating melting at 1200 degrees C, it cooled to the room temperature, the jet mill ground to 10 micrometers, and the two-component system metal fluoride was obtained. This two-component system metal fluoride 0.1 mass section was mixed with the carbonaceous aggregate 100 mass section of an example 5, the coal-tar pitch 100 mass section was added, after kneading, it calcinated at 950 degrees C after CIP shaping by 90MPa, and the two-component system metal fluoride content carbon burned product of 300x300x500 (mm) was obtained. The obtained burned product contained the two-component system metal fluoride 0.1%.

[0042] (Example 3 of a comparison) LiF whose mean particle diameter is 30 micrometers, and CaF2 whose mean particle diameter is 30 micrometers After mixing at a rate of 4:6 by the mole ratio and carrying out heating melting at 1200 degrees C, it cooled to the room temperature, the jet mill ground to 10 micrometers, and the two-component system metal fluoride was obtained. This two-component system metal fluoride 0.05 mass section was mixed with the carbonaceous aggregate 100 mass section of an example 5, the coal-tar pitch 100 mass section was added, after kneading, it calcinated at 950 degrees C after CIP shaping by 90MPa, and the two-component system metal fluoride content carbon burned product of 300x300x500 (mm) was obtained. The obtained burned product contained the two-component system metal fluoride 0.05%.

[0043] (Example 4 of a comparison) LiF whose mean particle diameter is 30 micrometers, and CaF2 whose mean particle diameter is 30 micrometers After mixing at a rate of 4:6 by the mole ratio and carrying out heating melting at 1200 degrees C, it cooled to the room temperature, the jet mill ground to 10 micrometers, and the two-component system metal fluoride was obtained. This two-component system metal fluoride 6 mass section was mixed with the carbonaceous aggregate 100 mass section of an example 3, the coal-tar pitch 100 mass section was added, after kneading, it calcinated at 950 degrees C after CIP shaping by 90MPa, and the two-component system metal fluoride content carbon burned product of 300x300x500 (mm) was obtained. The obtained burned product contained the two-component system metal fluoride 6%.

[0044] The carbon material test piece of 70x40x5 (mm) was cut down from the carbon burned product of the above-mentioned examples 1-12 and the examples 1-4 of a comparison, and the ACT-JP value was computed from the formula (2) which measured and mentioned above the weight decrement and bulk density of a test piece by the ACT-JP method in 90 degrees whenever [incident angle / of an alumina], and the formula (3). In addition, about the ACT-JP value, it considered as the following Measuring conditions.

Diameter of an injection nozzle : 5.2mm injection material : Alumina sample of 60 meshes : Carbon material test piece (70x40x5 (mm))

Air-current pressure : 5kg/cm2 injection material incident angle : The flow rate of 90 degree injection air current: Amount of 390cm3 / min injection material : Distance from 70g [/] time injection nozzle to a sample front face: 100mm result is collectively shown in Table 1.

[0045]

[Table 1]

		金属フッ化物		炭素電極中の含有率 (%)	かさ密度 (g/cm³)	ACT-JP値 (g/mm³) *1	F₂ 電解時		NF₃電解時		
		組成	混合比				電流密度*2 (A/dm²)	CF₄ 濃度*3	電流密度*2 (A/dm²)	CF₄ 濃度*3	電流効率 (%)
実施例1	一元系	−	−	0	1.58	0.34	△	○	×	○	−
実施例2					1.60	0.40	△	○	×	○	−
実施例3					1.65	0.44	△	○	×	○	−
実施例4					1.71	0.50	△	○	×	○	−
比較例1					1.33	0.16	○	×	×	×	−
実施例5	二元系	−	−	0	1.66	0.30	×	○	×	○	−
比較例2					1.52	0.17	×	×	×	×	−
実施例6	一元系	LiF-CaF₂	4:6	3	1.72	0.38	○	○	○	○	73.
実施例7		LiF-CaF₂	2:8	3	1.72	0.42	○	○	○	○	71
実施例8		LiF-MgF₂	4:6	3	1.73	0.34	○	○	○	○	70
実施例9	二元系	LiF-CaF₂	4:6	1	1.66	0.26	○	○	○	○	68
実施例10		LiF-CaF₂	4:6	3	1.65	0.25	○	○	○	○	72
実施例11		LiF-CaF₂	4:6	5	1.63	0.22	○	○	○	○	73
実施例12		LiF-CaF₂	4:6	0.1	1.65	0.27	○	○	○	○	65
比較例3		LiF-CaF₂	4:6	0.05	1.66	0.29	△	○	×	○	52
比較例4		LiF-CaF₂	4:6	6	1.62	0.16	○	×	○	×	73

*1. ACT-JP値は、噴射ノズル径52mm、噴射材60meshアルミナ、気流圧力5kg/cm²、噴射材入射角90°、噴射気流の流量390cm³/min、噴射量70g/回 ノズルから試料表面までの距離100mmで【0014】に示した式(2)及び式(3)より算出した。
*2. 電流密度評価 ○: 臨界電流密度 15A/dm²以上 △: 臨界電流密度 10〜15A/dm² ×: 臨界電流密度 10A/dm²以下
*3. CF₄ 濃度評価 ○: 発生ガス中のCF₄ 濃度が20ppm 以下 ×: 発生ガス中のCF₄ 濃度が20ppm 以上

[0046] The mimetic diagram of a measuring device is shown in drawing 2 . Using a carbon material test piece as 201 and an injection nozzle 202 among drawing 2 , theta is whenever [incident angle / of the injection material sprayed on a carbon material test piece].
[0047] The block of 210x80x20 (mm) was started from the carbon burned product of the above-mentioned examples 1-12 and the examples 1-4 of a comparison, and the two-component system metal fluoride content carbon material. They are F2 and NF3 about what covered 100 micrometers of nickel into the part used as the current-carrying part (busbar part) of the electrode about each block. It is used as an electrode for electrolysis, an electrolytic device uses the cell of 50A (A) capacity, and they are critical current density (the maximum current density which is the maximum current density which can carry out a seal of approval, and will

produce the anode effect if a seal of approval is carried out more than this), and CF4. It asked for concentration. CF4 Concentration is current density 5 A/dm3. Gas was extracted by the steady state and it measured with the gas chromatography. F2 At the time of generating, 90-degree C KF-2HF is used as the electrolytic solution, and it is NF3. At the time of generating, 120-degree C KF-NH4 F-2HF was used.
[0048] NF3 It is NF3 generated about electrolysis. Generation current efficiency was also searched for. A cell and the electrolytic solution used the same thing as the above mentioned thing. NF3 Generation current efficiency was searched for by the formula (10). A result is written together to Table 1.
Current efficiency (%) =-/(6x104 xRxI) .. (10)
Here, it is n:NF3. Reaction-electron several F:Faraday-constant P of a generation reaction: Pressure (atm)
V:NF3 Volume %f:NF3 Flow rate (10-3cm3 / min)
R: Gas constant (atm-cm3, deg-1, and mol-1)
T: Absolute temperature (K)
I: Consider as a current value (A) and it is NF3. The generation reaction was shown in the formula (7) and set to reaction electron (number n) =6.
[0049] The following thing can say from the above experimental result. It is the electrode in which the ACT-JP value carried out nickel covering at the current-carrying part of 0.2 or more carbon materials F2 Or NF3 When it uses for generating, it is CF4 in generation gas. Concentration was set to 20 ppm or less. Moreover, it is LiF-CaF2 of the mixed mole ratio of 4:6 to this carbon electrode. Or LiF-MgF2 It is the two-component system metal fluoride content carbon electrode of which 0.1-5 mass % addition was done F2 Or NF3 When it uses for generating, in any case, it is CF4 in generation gas. Concentration is set to 20 ppm or less, and, in any case, is 15 A/dm2. It turns out that it operates without moreover polarizing with the above high current density. Furthermore, this metal fluoride content carbon electrode is used, and it is NF3. NF3 at the time of making it generate Generating current efficiency was 70% or more of well head.
[0050]
[Effect of the Invention] It is CF4 by using the carbon electrode containing the carbon electrode or two-component system metal fluoride concerning this invention. F2 of few high grades Or NF3 It can manufacture. Moreover, it is NF3 about a two-component system metal fluoride content carbon electrode. By using for manufacture, the polarization by the anode effect can be controlled and it is NF3 at high current efficiency. It can also be made to generate.
[0051] Moreover, F2 of the amount which is the need by forming a generation gas storage means in the body of a cell and for which it asks by the way Or NF3 The so-called on-site-ization which can be supplied stably is attained. F2 [expensive] Or NF3 It having not only become unnecessary to purchase a spare bomb but Only an initial complement is F2 when required. Or NF3 Since gas can be supplied, it is F2 like before. Or NF3 It is not influenced by the amount of supply of gas, it forms successively to a semi-conductor manufacturing facility etc., and can be used suitably.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] Drawing 1 is F2 of this invention. Or NF3 It is the mimetic diagram of an on-site generator.
[Drawing 2] It is the mimetic diagram of the measuring device of the ACT-JP method.
[Description of Notations]
1 Body of Cell
2 Electrolytic Solution
3 Anode Plate
4 Anode Plate Generating Gas
5 Cathode
6 Hydrogen Gas
7 Nitrogen Gas Cylinder for Permutation
8 Hydrogen Generating Opening
9 Generation Generation-of-Gas Opening
10 Skirt Board
11 NaF -- Column
12 Anode Plate Room
13 Cathode Room
14 Rhine for Reduced Pressure
15 Pressure Regulating Valve
16, 19, 24, 27 Valve
17 25 Buffer tank
18 26 Pressure gage
20 Reduced Pressure Gas Outlet
21 Rhine for Pressurization
22 Pressure Regulating Valve
23 Pressurizer
28 Mass Flow
29 Pressurization Gas Outlet
30 Vacuum Pump
31 Cabinet
201 Carbon Material Test Piece
202 Injection Nozzle

[Translation done.]

* NOTICES *

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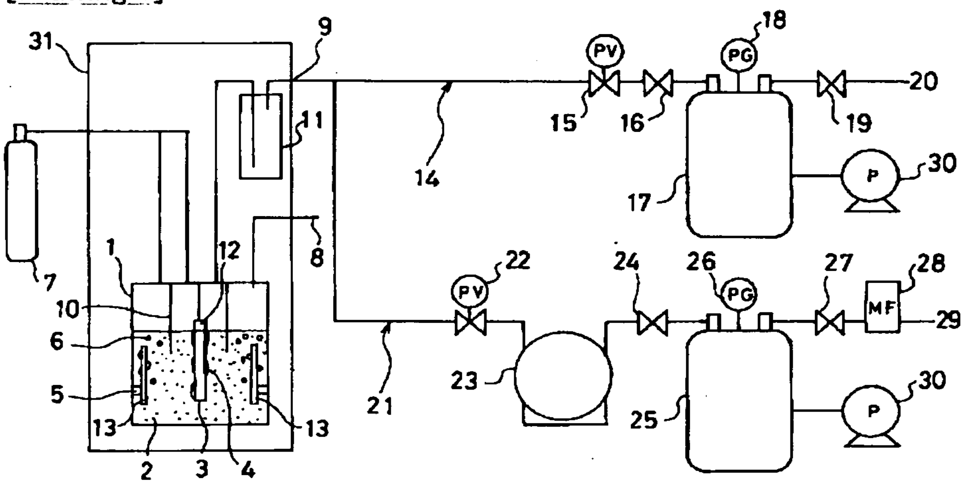
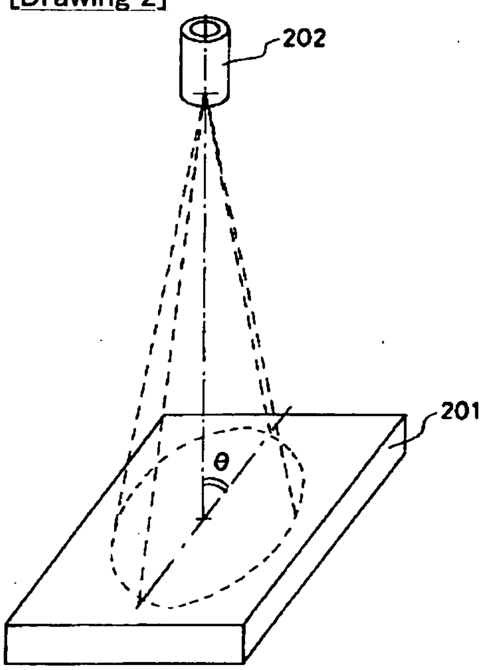
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]